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(54) Coextrusion binder compositions and coextruded multilayer composites using them

(57) Binder compositions for coextruded multilayer composites comprise:

- at least one component A chosen from (A1) graft polymers resulting from a grafting monomer (preferably maleic anhydride) and (a) impact or crystal styrene homo- and co-polymers and/or (b) optionally hydrogenated styrene - diene elastomer block polymers; (A2) a copolymer (b) mixed with a polymer (B1); (A3) graft polymers resulting from a grafting monomer and a mixture of a polymer (a) and at least one of (c) ethylene - vinyl acetate copolymers, ethylene - alkyl (meth)acrylate copolymers ethylene homopolymers and ethylene -  $\alpha$  - olefin copolymers; and (A4) graft polymers resulting from a grafting monomer and a polymer (a) to which at least one tackifying resin (d) has been added, these graft polymers being furthermore mixed with at least one polymer (B1); and optionally, at least one component B selected from (B1) graft polymers resulting from the grafting of a grafting monomer onto a polymer (c); and (B2) (ethylene -  $\alpha$  -olefin or vinyl acetate or alkyl (meth)acrylate - an abovementioned grafting monomer) terpolymers; and (C) the polymers (a), (b) and (c).

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COEXTRUSION BINDER COMPOSITIONS AND COEXTRUDED  
MULTILAYER COMPOSITES USING THEM

The present invention relates to a  
coextrusion binder composition and to coextruded  
5 multilayer composites in which the said composition is  
employed as adhesive layer.

Coextruded multilayer composites which have  
an outer layer of polystyrene, polycarbonate or  
polyester, especially polystyrene, are commonly  
10 employed for food containers such as cups and  
containers of the yogurt or compote pot type and the  
like, or for films such as thermoformed or heat-sealed  
lids. However, in these composites the outer layer is  
generally lined with a layer of ethylene - vinyl  
15 alcohol copolymer, polyamide, polyesteramide,  
polyolefin and the like, or of a mixture of these  
polymers, which have a poor affinity for it, with the  
result that provision must be made for an adhesive  
layer between the two. By way of examples of multilayer  
20 composites there may be mentioned those containing  
three layers (for example polyethylene/  
binder/polystyrene), or five layers (for example  
polyethylene/binder/ethylene - vinyl alcohol copolymer/  
binder/polystyrene) and the like.

25 The present invention also relates to  
composites formed by hot lamination or resin-coating, a  
technology according to which a multilayer including

the binder is extruded over a sheet of poly(methyl methacrylate), polystyrene, poly(ethylene terephthalate) and the like, the binder providing especially the adhesion to the sheet.

5           Many adhesive formulations have been developed for this purpose and are described in the literature. Most of these formulations include an ethylene - vinyl acetate copolymer grafted with maleic anhydride and/or styrene, in combination with another  
10       component which is especially an ungrafted ethylene - vinyl acetate copolymer, polystyrene, impact polystyrene, a petroleum resin and the like. The compositions described in US Patents No. 4 861 676 and No. 4 861 677 may be mentioned, among others.

15           French Patent Application No. 2 677 658 discloses an adhesive composition obtained by grafting an unsaturated carboxylic acid or a derivative thereof onto a mixture including 40 to 95 % by weight of ethylene - (meth)acrylic ester copolymer which has a  
20       (meth)acrylic ester content of 25 to 45 % by weight, 5 to 30 % by weight of polystyrene and 0 to 30 % by weight of a polymer which may be an ethylene - vinyl acetate copolymer.

          While, among the many resins presented in the  
25       literature, some are satisfactory from the viewpoint of adhesive performance, the latter must still be improved. In addition, the multilayer composites obtained very often do not cut out properly. Such

cutting out, generally carried out after the thermoforming or after the filling of the containers and fitting the lid, is performed either by pressure of a metal "net" on a table, or by shearing. If the cutting out is not correct, the thermoformed article remains attached to the sheet from which it has been formed. This gives rise to uncontrolled production stoppages and the changing of the cutter blades.

According to the present invention, there is provided a coextrusion binder composition which composition comprises:

- at least one polymer (A) chosen from:

(A1) graft polymers resulting from the grafting of at least one grafting monomer chosen from carboxylic acids containing ethylenic unsaturation, the corresponding acid anhydrides and derivatives of these acids and acid anhydrides, onto

(a) impact or crystal styrene homopolymers and copolymers; and/or

(b) styrene - diene elastomer block polymers and these same copolymers in the hydrogenated state, provided that (b) is not the only polymer in the mixture of (A) and optionally (B);

(A2) at least one copolymer (b) as defined above mixed with at least one polymer (B1) as defined below;

(A3) graft polymers resulting from the

cografting of at least one grafting monomer as defined above onto a mixture:

- of at least one polymer (a) as defined above; and
- 5 - of at least one polymer (c) chosen from ethylene - vinyl acetate copolymers, ethylene - alkyl (meth)acrylate copolymers, ethylene homopolymers and ethylene -  $\alpha$ -olefin copolymers, provided that the ethylene -  
10 alkyl (meth)acrylate copolymers may not represent more than 40 % by weight of the mixture subjected to cografting in the case of a polystyrene content lower than 30 % by weight if (A3) represents the major  
15 constituent of the binder composition; and (A4) graft polymers resulting from the cografting of at least one grafting monomer as defined above onto at least one polymer (a) as defined above, to which at least one tackifying resin (resin  
20 possessing adhesive bondability) (d) has been added, these graft polymers being furthermore mixed with at least one polymer (B1) as defined below; and optionally
  - at least one of:
  - 25 (B) polymers chosen from:  
(B1) graft polymers resulting from the grafting of at least one grafting monomer as defined above onto a polymer

- (c) chosen from ethylene - vinyl acetate copolymers, ethylene - alkyl(meth)acrylate copolymers, ethylene homopolymers and ethylene -  $\alpha$ -olefin copolymers; and
- (B2) (ethylene -  $\alpha$ -olefin or vinyl acetate or alkyl (meth)acrylate - monomer of the type of the abovementioned grafting monomers) terpolymers; and
- (C) polymers (a), (b) and (c) as defined above.

The compositions according to the invention have adhesive performances that are correct, or even superior to those of the known compositions, but can offer the additional advantage of allowing a greater ease of cutting out than the known compositions.

In general, each of the graft polymers (A1), (B1), the cografterd copolymers (A3) and all the polymers comprising a cografterd resin (d), included within the formulations of the compositions of the invention, comprise from 0.005 to 5 % by weight of units originating from the grafting monomer(s) relative to the polymer or to the mixture of polymers subjected to grafting. The grafting monomers are chosen especially from (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride or a substituted maleic anhydride, such as dimethylmaleic anhydride or a salt,

amide, imide or ester of a carboxylic acid containing ethylenic unsaturation, such as mono- and disodium maleate, acrylamide, maleimide and diethyl fumarate. Maleic anhydride and maleic acid are preferred.

5           The grafting may be performed by known methods comprising melting the polymer(s) to be grafted, adding thereto the grafting monomer and from 50 to 20 000 ppm, relative to the polymer(s), of a radical polymerization initiator, mixing so as to  
10 obtain a uniform distribution of the grafting monomer and of the initiator in the polymer(s), kneading the resulting mixture in an extruder at a temperature above the melting point of the polymer(s), extruding the resulting graft polymer as a shaped article, tablets or  
15 other forms which are subsequently employed as such or as a mixture with other polymers, for the coextrusion of multilayer structures, as will be described below.

          Apart from this grafting in an extruder, another possible grafting method which may also be  
20 mentioned is grafting in solution, comprising dissolving the polymer(s) to be grafted in a solvent and adding thereto the grafting monomer(s) and the initiator to perform the graft polymerization at a temperature of between 80 and 150°C.

25           The free radical initiator used may belong to different classes which are well known to a person skilled in the art. Among these there may be mentioned peroxides, peresters, hydroperoxides and diazo



compounds. Peroxides which may be mentioned are dicumyl peroxide, di-tert-butyl peroxide, benzoyl peroxide, lauroyl peroxide,  $\alpha, \alpha'$ -bis(t-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane and 2,5-dimethyl-2,5-di(t-butylperoxy)-3-hexyne. Tertiary butyl perbenzoate may be mentioned as perester, t-butyl hydroperoxide and cumene hydroperoxide as hydroperoxide, and azobisisobutyronitrile as diazo compound.

The grafting may be performed, for example on a polystyrene, and then, if appropriate, the resulting graft polymer may be "diluted" with at least one other polymer, which itself may be grafted. Alternatively cografting, for example, on a polystyrene and an ethylene - vinyl acetate copolymer, may be used. This offers the advantage of simplifying manufacture, since the required composition is obtained directly if the cografting is not followed by dilution.

The polymers (a) used within the composition according to the invention include styrene homopolymers and copolymers (crystal polymers) and polystyrenes containing rubbery components (impact polymers), in particular those referred to as high-impact.

Examples of styrene copolymers which may be mentioned are chloropolystyrene, poly- $\alpha$ -methylstyrene, styrene - chlorostyrene copolymers, styrene - propylene copolymers, styrene - butadiene copolymers, styrene - isoprene copolymers, styrene - vinyl chloride

copolymers, styrene - vinyl acetate copolymers, styrene - alkyl acrylate (methyl, ethyl, butyl, octyl, phenyl acrylate) copolymers, styrene - alkyl methacrylate (methyl, ethyl, butyl, phenyl methacrylate) copolymers, styrene - methyl  $\alpha$ -chloroacrylate copolymers and styrene - acrylonitrile - alkyl acrylate copolymers. The comonomer content in these copolymers generally ranges up to 20 % by weight.

10           The polystyrenes containing rubbery components are preferably those containing from 1 to 20 % by weight of units originating from the rubbery components which are, for example, butadiene and isoprene.

15           The copolymers (b) are the abovementioned block copolymers obtained by copolymerization of styrene and of a diene such as butadiene and isoprene. Diblock styrene - butadiene and styrene - isoprene and triblock styrene - butadiene - styrene and styrene - isoprene - styrene copolymers may be mentioned. Their preparation enables linear or branched products to be obtained. These same copolymers may be hydrogenated. SEBSs or SEPSs are thus obtained, depending on whether SBSs or SISs are employed as base for the

20           hydrogenation. The styrene content of these copolymers is generally lower than or equal to 50 % by weight. The styrene/diene weight ratios are especially between 10/90 and 50/50.

The polymers (c), included within the definition of the component (A3), are especially:

- ethylene - vinyl acetate copolymers which have a vinyl acetate content generally lower than 60 % by weight, preferably lower than 50 % by weight;
- ethylene homopolymers and copolymers of ethylene and of at least one alpha-olefin (all copolymers commonly denoted by PE, LDPE, LLDPE, VLDPE, HDPE and EPR). The alpha-olefin generally contains 3 to 12 carbon atoms and is chosen especially from propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene and their mixtures. The content of units derived from ethylene is generally at least 40 % by weight and the relative density of these homo- and copolymers is generally between 0.880 and 0.970;
- ethylene - alkyl, in particular  $C_1$ - $C_{12}$  alkyl, (meth)acrylate copolymers which have a (meth)acrylate content generally of between 5 and 60 % by weight, preferably between 7 and 40 % by weight; methyl, ethyl and butyl (meth)acrylates may be mentioned as alkyl (meth)acrylates.

Furthermore, a quantity of at least one resin which has an adhesive bondability (d) may be added to

at least one of the polymers or mixtures of polymers subjected to a grafting or to a cografting, in order to lead to a grafting or cografting product included within the composition of the invention.

5           As tackifying resins (d) which may be included within the composition of the coextrusion binder according to the invention in the cografted state, there may be mentioned styrene-based resins such as poly- $\alpha$ -methylstyrene resins, rosin resins, rosin ester resins, aliphatic petroleum resins and terpene, 10 terpene-phenolic, coumarone and coumarone-indene aromatic resins. These resins generally cannot represent more than 40 % by weight of the composition. The content of these tackifying resins in the 15 composition, which depends on the required melt index, does not preferably exceed 10 % by weight. Furthermore, some may be hydrogenated, such as rosin resins, aliphatic petroleum resins and terpene resins.

          Compositions according to the invention which 20 have been found particularly advantageous are the following (the total composition representing 100 % by weight each time):

- compositions consisting of:
  - 5 to 70 % by weight, in particular 25 5 to 45 % by weight, of at least one polystyrene consisting of at least one impact or crystal polystyrene grafted with optionally ungrafted impact polystyrene, the

latter, if present, representing up to 40 %  
by weight of the composition; and

- 30 to 95 % by weight, in particular  
55 to 95 % by weight, of an ethylene - vinyl  
acetate copolymer grafted with maleic  
anhydride, of an ethylene -alkyl  
(meth)acrylate graft copolymer grafted with  
maleic anhydride, or of an (ethylene - vinyl  
acetate or alkyl (meth)acrylate - maleic  
anhydride) terpolymer,  
optionally mixed with impact or crystal  
polystyrene and/or an ethylene - vinyl acetate  
copolymer and/or an ethylene - alkyl  
(meth)acrylate copolymer;

- compositions consisting of the product  
of cograftering of maleic anhydride onto a mixture  
of:

- 5 to 70 % by weight, in particular  
5 to 45 % by weight, of at least one impact  
or crystal polystyrene; and

- 30 to 95 % by weight, in particular  
55 % to 95 % by weight, of an ethylene -vinyl  
acetate copolymer and/or of an ethylene -  
alkyl (meth)acrylate copolymer, the  
condition indicated in the case of (A3) being  
furthermore complied with,  
optionally mixed with impact or crystal

polystyrene and/or an ethylene - vinyl acetate

copolymer and/or an ethylene - alkyl  
(meth)acrylate copolymer;

- compositions consisting of:

5                   - 10 to 40 % by weight of the product  
of cografting of maleic anhydride onto a  
mixture of impact polystyrene and of a minor  
quantity of an alpha-methylstyrene tackifying  
resin; and

10                   - 60 to 90 % by weight of ethylene -  
vinyl acetate graft or ethylene - methyl  
(meth)acrylate graft copolymer; and

- compositions consisting of:

15                   - 10 to 30 % by weight of a styrene -  
butadiene - styrene block copolymer; and  
- 70 to 90 % by weight of ethylene -  
vinyl acetate copolymer grafted with maleic  
anhydride.

The binder composition according to the  
invention may be used to form a multilayer composite by  
20 a method comprising providing a layer of the binder  
composition between a layer of polystyrene,  
polycarbonate or polyester and at least one resin  
chosen from polyolefins, ethylene-vinyl alcohol  
copolymers, polyamides and polyesters.

25                   The present invention also provides a  
coextruded multilayer composite including at least once  
the following succession of three layers:

- a layer of polystyrene, polycarbonate,

or polyester,

- a layer of the coextrusion binder composition as defined above; and

- a layer consisting of at least one resin chosen from polyolefins, ethylene - vinyl alcohol copolymers, polyamides and polyesters.

The following layer combinations may be mentioned in particular:

PS/binder/EVOH, PS/binder/PA, PS/binder/PET,  
 10 PS/binder/PO, PS/binder/EVOH/binder/PS, PS/binder/EVOH/  
 binder/PO, PS/binder/EVOH/binder/PET and  
 PS/binder/EVOH/PA/binder/PS, where PS = polystyrene,  
 EVOH = ethylene-vinyl alcohol copolymer, PA =  
 polyamide, PET = poly(ethylene terephthalate) and PO =  
 15 polyolefin.

The polystyrenes PS are as defined above.

Polyolefins PO here include an ethylene -  
 $\alpha$ -olefin copolymer, an ethylene - vinyl acetate  
 copolymer, ethylene - alkyl (meth)acrylate copolymers  
 20 which have an alkyl (meth)acrylate content lower than  
 25 % by weight, low-density polyethylenes, high-density  
 polyethylenes, polypropylenes and mixtures of these  
 polymers.

Ethylene - vinyl alcohol EVOH copolymers  
 25 include saponified ethylene - vinyl acetate copolymers  
 which have a degree of saponification of at least  
 50 mol%. It is preferable that these polymers should  
 contain at least 30 mol% of vinyl alcohol units, to

obtain good adhesiveness and gas impermeability properties.

The polyamides PA are linear polymers containing acid amide bonds, obtained by condensation of diamines and dicarboxylic acids, condensation of aminoacids or decyclization of lactams. Representative examples of these polyamides are nylon 6, nylon 6-6, nylon 6-10, nylon 11 and nylon 12.

The polyesters employed in the coextruded composites of the present invention are polymers obtained by condensation of saturated diacids and of glycols. It is possible to mention in particular poly(ethylene terephthalate) obtained from ethylene glycol and terephthalic acid, poly(ethylene terephthalate) copolymers which have, as copolymerization component, a saturated diacid such as phthalic acid, isophthalic acid, sebacic acid, adipic acid, azelaic acid, glutamic acid, succinic acid, oxalic acid and the like, poly(ethylene terephthalate) copolymers which have, as copolymerization component, a diol such as 1,4-cyclohexanedimethanol, diethylene glycol, propylene glycol and the like, and mixtures of these polymers.

The thickness of the composite of the present invention is generally from 100  $\mu\text{m}$  to 3 mm, preferably 500  $\mu\text{m}$  to 2 mm. In the case of the composite containing three layers of polystyrene/binder/sealing material (such as a low-density polyethylene, a linear low-



density polyethylene, an ethylene - vinyl acetate copolymer and the like), the thickness of the composite is generally from 100 to 1000  $\mu\text{m}$ , preferably 100 to 600  $\mu\text{m}$ . The thickness of the polystyrene layer in the composite according to the present invention suitably represents 30 to 96 %, preferably 60 to 90 %, of the total thickness of the laminate. The thickness of the binder composition layer suitably represents 1 to 35 %, preferably 2 to 20 %, of the total thickness of the composite, and the thickness of the sealing material layer suitably represents 1 to 35 %, preferably 2 to 20 %, of the total thickness of the composite.

The peel strength of the composites of the present invention, in the case where the thickness of the binder layer is 30  $\mu\text{m}$ , may be above 6 N/15 mm, generally at least 9 N/15 mm.

The binder compositions according to the present invention and the multilayer composites employing these compositions have excellent properties of adhesive strength and of resistance to separation of the layers after coextrusion, as well as excellent cutting-out properties, with the result that they are very useful for food containers and the like.

The following examples illustrate the invention without, however, limiting its scope. In these examples the percentages are given by weight unless indicated otherwise. The particular compositions of coextrusion binders used in these examples belong to

types II to IX, detailed in Table 1 below, type I representing the reference composition. In this table the constituents are indicated, the following abbreviations being employed:

5	PS	:	polystyrene
	EVA copo	:	ethylene - vinyl acetate copolymer
	EMA copo	:	ethylene - methyl acrylate copolymer
	EVA/MA terpo	:	ethylene - vinyl acetate - maleic anhydride terpolymer
10	EBA/MA terpo	:	ethylene - butyl acrylate - maleic anhydride terpolymer
	g MA	:	grafted with maleic anhydride.

Table 1

Coextrusion binder composition type	Components		
	(A)	(B)	(C)
I (reference)		EVA copo g MA	
II	impact PS g MA	EVA copo g MA	impact PS
III	impact PS g MA	EVA copo g MA	
IV	SBS block copo + EVA copo g MA		
V	impact PS g MA	EMA copo g MA	
VI	impact PS g MA	EBA or EVA/MA terpo	
VII	impact PS g MA + crystal PS g MA	EVA copo g MA	
VIII	(impact PS + poly- $\alpha$ - methylstyrene resin) g MA	EVA copo g MA	
IX	(impact PS + EVA copo) g MA		
X	(crystal PS + EVA copo) g MA		

Furthermore, the particular constituents below were used in these examples (see also first column of Table 2). The constituent unit contents of the various graft copolymers are here weight contents

measured by FTIR spectroscopy; the melt indices, expressed in g/10 min, were measured according to ASTM standard D-1238 in condition (L) (23°C, 2.16 kg) in the case of impact PS, crystal PS and in condition (E) (190°C, 2.16 kg) in the case of impact PS g MA, crystal PS g MA and other copolymers and terpolymers; the Izod impact strength was measured according to ISO standard 180/1A, and the Vicat softening temperature according to ISO standard 306 B.

The melting points were obtained according to the ATD method.

#### Individual constituents used

The impact PSs 1, 2, 3 and 4 and the crystal PS employed in the examples are polystyrenes marketed under the series name "Lacqrène" by the company Elf Atochem S.A. Their characteristics are given in Table 2 below:

Table 2

PS	Lacqrène	Melt index (g/10 min)	Izod impact strength (kJ/m <sup>2</sup> )	Vicat softening temperature (°C)
impact 1	8350	4.5	13	85
impact 2	7240	4.5	11	87
impact 3	5240	4.5	13	85
impact 4	3351	4.5	8	94
crystal	1160	2.5		98

Preparation of impact PS 1 g MA (Lacqrène  
8350 g MA)

Lacqrène 8350 impact polystyrene and maleic anhydride, in a ratio of 1.5 % by weight relative to the impact polystyrene, are introduced into a  
5 corotative twin-screw extruder of Werner 30 type (12 barrels, 30 mm diameter). 8500 ppm of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (Trigonox 101) are injected sideways into the extruder at barrel No. 4. The barrel  
10 temperatures displayed are between 180°C (barrel No. 1) and 210°C (barrel No. 10). The stock temperature is approximately 200°C. The residues of free maleic anhydride are removed by degassing at barrel No. 10. The overall throughput of the extruder is 20 kg/hour  
15 and the speed of rotation of the screws 280 rev/min. Impact polystyrene grafted with 0.9 % of maleic anhydride and exhibiting a melt index of 3.2 is obtained.

Preparation of impact PS 2 g MA (Lacqrène  
20 7240 g MA)

The procedure is as for the preparation of impact PS 1 g MA, except that impact PS 2 is employed. The polymer obtained is an impact polystyrene grafted with 0.96 % of maleic anhydride and exhibiting a melt  
25 index of 3.3.

Preparation of impact PS 3 g MA (Lacqrène  
5240 g MA)

The procedure is as for the preparation of

impact PS 1 g MA, except that impact PS 3 and 15 000 ppm of Trigonox 101 are employed. The polymer obtained is an impact polystyrene grafted with 1.2 % of maleic anhydride and with a melt index of 3.1.

5                    Preparation of crystal PS g MA (Lacqrène 1160 g MA)

The procedure is essentially as for the preparation of impact PS 1 g MA, except that Lacqrène 1160 crystal PS is employed. The proportion of maleic anhydride introduced is 1.5 % by weight, and 1.1 % by weight of Trigonox 101 is injected sideways, these quantities being in relation to the crystal PS. The speed of rotation of the screws is 130 rev/min and the throughput is 10 kg/hour. Crystal polystyrene grafted with 0.98 % of maleic anhydride, with a melt index of 3.3, is obtained.

Preparation of EVA copo g MA

Into the hopper of a corotative twin-screw extruder of Werner 30 type (see above) are introduced: an ethylene - vinyl acetate copolymer (vinyl acetate content: 28 % by weight, melt index: 4), maleic anhydride in a proportion of 0.25 % relative to the EVA copolymer, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (Luperox 101) in a proportion of 200 ppm relative to the EVA copolymer. The displayed temperatures of the barrels are between 170°C (barrel No. 1) and 220°C (barrel No. 8). The stock temperature is approximately 200°C. The residues of free maleic anhydride are

removed by degassing at barrel No. 10. The overall throughput of the extruder is 15 kg/hour. An EVA copolymer grafted with 2000 ppm of maleic anhydride is obtained, exhibiting a melt index of 3 to 3.5, a melting point of 75°C and a Vicat softening point of 51°C.

Preparation of EMA copolymer

Into the hopper of a corotative twin-screw extruder of Werner 30 type (see above) are introduced: an ethylene - methyl acrylate copolymer (methyl acrylate content: 29 %, melt index: 3.1), maleic anhydride in a proportion of 0.5 % relative to the EMA copolymer, and Luperox 101 in a proportion of 150 ppm relative to the EMA copolymer. The stock temperature is approximately 200°C. The residues of free maleic anhydride are removed by degassing in line. The expected polymer is obtained, that is an EMA grafted with 2300 ppm of maleic anhydride and exhibiting a melt index of 2.5, a melting point of 66°C and a Vicat softening point lower than 40°C.

The EVA copolymer employed in the examples, marketed by the company Elf Atochem S.A. under the name "Evatane 2805", has a vinyl acetate content of 27-29 % by weight, a melt index of 5-8 g/10 min, a melting point of 73°C and a Vicat softening point of 43°C.

The SBS block copolymer employed in the examples is the styrene - butadiene - styrene triblock linear copolymer marketed under the name

"Cariflex KX 139".

The poly- $\alpha$ -methylstyrene resin employed in the examples is the resin marketed by the company DSM under the name "Kristallex F 120".

5           The EVA/MA terpolymer employed in the examples is an ethylene - vinyl acetate - maleic anhydride terpolymer which has a melt index of 7 g/10 min and a vinyl acetate weight content of 26 %.

10           The EBA/MA terpolymer employed in the examples, marketed by Elf Atochem S.A. under the name "Lotader 3700" is an ethylene - butyl acrylate - maleic anhydride terpolymer which has a melt index of 6 g/10 min and a butyl acrylate weight content of 30 %.

15           Examples 1 to 25 which follow illustrate the preparation of binder compositions for reference and according to the invention (Examples 2 to 25). These compositions have been evaluated for adhesiveness after coextrusion at 220°C of a five-layered sheet with a total thickness of 790 microns and which has the  
20           characteristics reported in Table 3, which follows:



Table 3

Layer number	Layer composition	Trade name	Thickness ( $\mu\text{m}$ )
1	impact PS	Lacqrène 8350 (Elf Atochem S.A.)	600
2	Binder subjected to the test		30
3	EVOH copo (ethylene - vinyl alcohol copolymer containing 62 mol% of vinyl alcohol)	Soarnol ET	30
4	Binder subjected to the test		30
5	Low density PE	Lacqtène 1020 FN 24 (Elf Atochem S.A.)	100

For the evaluation of adhesiveness, the peeling is conducted in a laboratory conforming to the standards of a materials evaluation laboratory, according to NFT standard 76-112 part 2, but with the following modifications: a peeling angle of 90 instead of 180 and test piece width of 15 mm instead of 25 mm.

The test pieces are taken from the middle of the coextruded sheets, in the direction of extrusion. The peeling speed is 200 mm/minute. The determination of the peel strengths, on the recordings obtained, is performed according to ISO standard 6133. The

reproducibility of the complete sequence (coextrusion/peeling) was verified by employing the same binder a number of times on different days and at different times.

5                   Example 1 (reference example)

The five-layered sheet described above was produced with EVA copolymer MA as binder. This example illustrates what it is possible to obtain in terms of peel strength.

10                   Example 2

A mixture prepared by dry mixing of granules which have the weight composition reported in Table 5 is introduced into the hopper of a Buss PR 46/70 co-kneader ( $L/D = 11$ ), fitted with a recycle screw. The overall throughput of the plant is 25 kg/h, the speed of rotation of the kneader is 200 rev/min and the stock temperatures between 200°C and 205°C. The speed of rotation of the recycle screw is 33 rev/min. Vacuum is applied at well No. 3 of the co-kneader. The compound obtained has a melt index of 2.6. It is subsequently employed in a five-layered composite prepared as shown above. The peel strengths are reported in Table 5.

Examples 3 to 16

The procedure is as in Example 2, the constituents being varied in their nature and their proportion as shown in Table 5. The results, shown in this same table, in terms of peel strength, are superior to those of reference Example 1.

Example 17

EVA copo g MA and a "cograft" (impact PS 1 + poly- $\alpha$ -methylstyrene resin) g MA, prepared as described in the following example, are mixed as in Example 2.

5 The peel strength results are shown in Table 5.

Example 18

Into a corotative twin-screw extruder of Werner type (12 barrels) is introduced a mixture of granules consisting of 30 % by weight of impact PS 4 and 70 % by weight of EVA copo, 0.5 % by weight of maleic anhydride and 150 ppm of Luperox 101 on a polyethylene powder carrier. The mixture is extruded at a throughput of 15 kg/hour (200 rev/min) and at a stock temperature of approximately 210°C. The volatile substances (ungrafted maleic anhydride and peroxide residues) are degassed in line at barrel No. 10 of the extruder. The "co-graft" obtained at the extruder exit has a melt index of 2.2 and a graft content of 1600 ppm of grafted MA. The binder thus obtained is introduced into a five-layered composite and then coextruded as shown in Example 2. The peel strengths obtained are reported in Table 5.

Examples 19 to 25

The procedure is as in Example 18, but with the variants reported in Tables 4 and 5 below. Table 5 gives the composition and the results relating to the peel strengths.

Table 4

Example	% of maleic anhydride introduced	Quantity of organic peroxide introduced (ppm)	Extrusion through-put (kg/h)	Melt index of the co-graft obtained (g/10 min) (190°C, 2.16 kg)	Grafting content (ppm of MA)
19	0.5	150	15	1.8	2500
20	0.375	114	20	2.8	2000
21	0.5	150	15	3.8	3300
22	0.5	150	15	4	2700
23	0.5	150	15	3.6	4000
24	0.5	150	15	3	3300
25	0.375	114	20	3.3	1700

Table 5

Type	Constituents of the extrusion binder		COMPOSITION TYPE					
			I	II		III		
	Example		1 (Ref)	2	3	4	5	6
A1	Impact PS 1 g MA (Lacqrene 8350 g MA)			5	25	5	10	
A1	Impact PS 2 g MA (Lacqrene 7240 g MA)							
A1	Impact PS 3 g MA (Lacqrene 5240 g MA)							10
A1	Crystal PS g MA (Lacqrene 1160 g MA)							
B1	EVA copo g MA		100	70	70	60	90	90
B1	EMA copo g MA							
B2	EVA/MA terpo							
B2	EBA/MA terpo (Lotader 3700)							
a	Impact PS 1 (Lacqrene 8350)			25	5	35		
a	Impact PS 4 (Lacqrene 3351)							
a	Crystal PS (Lacqrene 1160)							
b	SBS block copo (Cariflex KX 139)							
c	EVA copo (Evatane 2805)							
d	Poly- $\alpha$ -methylstyrene resin (Kristallex F120)							
	Peel strength (in N/15 mm)	t0+8 days	7.22-7.82	16.67	12.75	22.06	10.79	16.61
		t0+1 month	6.65-7.37	19.62	19.62	18.72	7.33	16.31
		t0+2 months	6.51-7.35	18.85	20.33	20.29	9.81	16.65

Table 5 Continued

Type	Constituents of the extrusion binder		COMPOSITION TYPE					
			III Continued					IV
	EXAMPLE		7	8	9	10	11	12
A1	Impact PS 1 g MA (Lacqrene 8350 g MA)		20	25			30	
A1	Impact PS 2 g MA (Lacqrene 7240 g MA)				25			
A1	Impact PS 3 g MA (Lacqrene 5240 g MA)					25		
A1	Crystal PS g MA (Lacqrene 1160 g MA)							
B1	EVA copo g MA		80	75	75	75	70	80
B1	EMA copo g MA							
B2	EVA/MA terpo							
B2	EBA/MA terpo (Lotader 3700)							
a	Impact PS 1 (Lacqrene 8350)							
a	Impact PS 4 (Lacqrene 3351)							
a	Crystal PS (Lacqrene 1160)							
b	SBS block copo (Cariflex KX 139)							20
c	EVA copo (Evatane 2805)							
d	Poly- $\alpha$ -methylstyrene resin (Kristallex F120)							
	Peel strength (in N/15 mm)	t0+8 days	18.63	19.31	21.56	11.17	9.81	9.41
		t0+1 month	18.05	21.56	24.12	10.98	12.75	9.81
		t0+2 months	19.32-21.09	22.75	21.48	10.81	4.41	10.78

Table 5 Continued

Type	Constituents of the extrusion binder		COMPOSITION TYPE					
			V	VI		VII	VIII	IX
	EXAMPLE		13	14	15	16	17	18
A1	Impact PS 1 g MA (Lacgrene 8350 g MA)		30	30	30	15		
A1	Impact PS 2 g MA (Lacgrene 7240 g MA)							
A1	Impact PS 3 g MA (Lacgrene 5240 g MA)							
A1	Crystal PS g MA (Lacgrene 1160 g MA)					15		
B1	EVA copo g MA					70	70	
B1	EMA copo g MA		70					
B2	EVA/MA terpo			70				
B2	EBA/MA terpo (Lotader 3700)				70			
a	Impact PS 1 (Lacgrene 8350)						27°	
a	Impact PS 4 (Lacgrene 3351)							30°
a	Crystal PS (Lacgrene 1160)							
b	SBS block copo (Cariflex KX 139)							
c	EVA copo (Evatane 2805)							70°
d	Poly- $\alpha$ -methylstyrene resin (Kristallex F120)						3°	
	Peel strength (in N/15 mm)	t0+8 days	6.18	9.81	10.79	7.16	14.71	15.15
		t0+1 month	6.86	8.82	7.84	7.84	11.77	22.01
		t0+2 months	9.41	7.84	9.16	6.86	12.75	23.74

Table 5 Continued

Type	Constituents of the extrusion binder		COMPOSITION TYPE						
			IX Continued						X
	EXAMPLE		19	20	21	22	23	24	25
A1	Impact PS 1 g MA (Lacqrene 8350 g MA)								
A1	Impact PS 2 g MA (Lacqrene 7240 g MA)								
A1	Impact PS 3 g MA (Lacqrene 5240 g MA)								
A1	Crystal PS g MA (Lacqrene 1160 g MA)								
B1	EVA copo g MA								
B1	EMA copo g MA								
B2	EVA/MA terpo								
B2	EBA/MA terpo (Lotader 3700)								
a	Impact PS 1 (Lacqrene 8350)				20°	10°	30°	40°	
a	Impact PS 4 (Lacqrene 3351)		40°	15°					
a	Crystal PS (Lacqrene 1160)								15°
b	SBS block copo (Cariflex KX 139)								
c	EVA copo (Evatane 2805)		60°	85°	80°	90°	70°	60°	85°
d	Poly- $\alpha$ -methylstyrene resin (Kristallex F120)								
	Peel strength (in N/15 mm)	t0+8 days	8.21	15.20	16.07	15.24	17.88	14.07	7.84-16.67
		t0+1 month	8.44	9.32	14.61	13.73	17.67	14.42	6.86-17.65
		t0+2 months	9.84	15.08	15.16	13.27	19.70	14.98	18.89

\* cografting - cografting product entering within component A4 in the case of Example 17

\* cografting - component A3 in the case of Examples 18 to 25



CLAIMS

1. A binder composition which composition comprises:

- at least one polymer (A) chosen from:

5 (A1) graft polymers resulting from the grafting of at least one grafting monomer chosen from carboxylic acids containing ethylenic unsaturation, the corresponding acid anhydrides and derivatives of these acids and acid anhydrides, onto

10 (a) impact or crystal styrene homopolymers and copolymers; and/or  
(b) styrene - diene elastomer block polymers and these same copolymers in the hydrogenated state, provided that (b) is  
15 not the only polymer in the mixture of (A) and optionally (B);

(A2) at least one copolymer (b) as defined above mixed with at least one polymer (B1) as defined below;

20 (A3) graft polymers resulting from the cograftering of at least one grafting monomer as defined above onto a mixture:

- of at least one polymer (a) as defined above; and

25 - of at least one polymer (c) chosen from ethylene - vinyl acetate copolymers, ethylene - alkyl (meth)acrylate copolymers,

ethylene homopolymers and ethylene - $\alpha$ -olefin copolymers, provided that the ethylene - alkyl (meth)acrylate copolymers may not represent more than 40 % by weight of the mixture subjected to cografting in the case of a polystyrene content lower than 30 % by weight if (A3) represents the major constituent of the binder composition; and (A4) graft polymers resulting from the cografting of at least one grafting monomer as defined above onto at least one polymer (a) as defined above, to which at least one tackifying resin (d) has been added, these graft polymers being furthermore mixed with at least one polymer (B1) as defined below; and optionally

- at least one of:
  - (B) polymers chosen from:
    - (B1) graft polymers resulting from the grafting of at least one grafting monomer as defined above onto a polymer (c) chosen from ethylene - vinyl acetate copolymers, ethylene - alkyl (meth)acrylate copolymers, ethylene homopolymers and ethylene -  $\alpha$ -olefin copolymers; and
    - (B2) (ethylene -  $\alpha$ -olefin or vinyl acetate or alkyl (meth)acrylate - monomer of the type of the abovementioned grafting

monomers) terpolymers; and

(C) polymers (a), (b) and (c) as defined above.

2. A composition according to Claim 1,  
5 wherein each graft or cografted polymer comprises from 0.005 to 5 % by weight of units originating from the grafting monomer(s).

3. A composition according to Claim 1 or 2,  
wherein the grafting monomer(s) is/are chosen from  
10 (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, itaconic anhydride, maleic anhydride or a substituted maleic anhydride, such as dimethylmaleic anhydride or a salt, amide, imide or ester of a carboxylic acid containing ethylenic  
15 unsaturation.

4. A composition according to Claim 3,  
wherein the salt, amide, imide or ester is chosen from mono- and disodium maleate, acrylamide, maleimide and diethyl fumarate.

20 5. A composition according to Claim 1 or 2,  
wherein the grafting monomer(s) is/are chosen from maleic anhydride and maleic acid.

6. A composition according to any preceding Claim, wherein the polymer(s) (a) is/are chosen from  
25 styrene homopolymers, styrene copolymers and styrene polymers containing rubbery components, which have from 1 to 20 % by weight of units originating from the rubbery components.

7. A composition according to any preceding Claim, wherein the block copolymer(s) is/are chosen from styrene - butadiene, styrene - isoprene, styrene - butadiene - styrene and styrene - isoprene - styrene copolymers, the styrene/diene weight ratios being between 10/90 and 50/50.

8. A composition according to any preceding Claim, wherein the ethylene - vinyl acetate copolymer (c) has a vinyl acetate content lower than 60 % by weight.

9. A composition according to any preceding Claim, wherein at least one tackifying resin (d) is added to at least one of the polymers or polymer mixtures subjected to grafting or to cograftering to form a grafted or cograftered product within the composition.

10. A composition according to Claim 9, wherein the tackifying resin (d) is chosen from  $\alpha$ -methylstyrene resins, optionally hydrogenated rosin resins, rosin ester resins, optionally hydrogenated aliphatic petroleum resins, optionally hydrogenated terpene resins and terpene-phenolic, coumarone and coumarone-indene aromatic resins.

11. A composition according to Claim 9 or 10, wherein the tackifying resin content does not exceed 40 % by weight of the total composition.

12. A composition according to Claim 9 or 10, wherein the tackifying resin content does not exceed 10 % by weight of the total composition.

13. A composition according to any of Claims 1 to 12, which consists of:

- 5 to 70 % by weight of at least one polystyrene consisting of at least one impact or crystal polystyrene grafted with optionally ungrafted impact polystyrene, the latter, if present, representing up to 40 % by weight of the composition; and
  - 30 to 95 % by weight of an ethylene - vinyl acetate copolymer grafted with maleic anhydride, of an ethylene - alkyl (meth)acrylate copolymer grafted with maleic anhydride, or of an ethylene - vinyl acetate or alkyl (meth)acrylate - maleic anhydride terpolymer,
- optionally mixed with impact or crystal polystyrene and/or an ethylene - vinyl acetate copolymer and/or an ethylene - alkyl (meth)acrylate copolymer.

14. A composition according to any of Claims 1 to 12, which consists of the product of cografting maleic anhydride onto a mixture of:

- 5 to 70 % by weight of at least one impact or crystal polystyrene; and
- 30 % to 95 % by weight of an ethylene - vinyl acetate copolymer and/or of an ethylene - alkyl (meth)acrylate copolymer, the condition indicated in Claim 1 in the definition of (A3) being complied with,

optionally mixed with impact or crystal polystyrene and/or an ethylene - vinyl acetate copolymer and/or an ethylene - alkyl (meth)acrylate copolymer.

5                   15. A composition according to any of Claims 1 to 12, which consists of:

- 10 to 40 % by weight of the product of  
          cografting of maleic anhydride onto a mixture  
          of impact polystyrene and of a minor quantity  
10           of an alpha-methylstyrene tackifying resin;  
          and
- 60 to 90 % by weight of ethylene - vinyl  
          acetate graft or ethylene - methyl  
          (meth)acrylate graft copolymer.

15                   16. A composition according to any of Claims 1 to 12, which consists of:

- 10 to 30 % by weight of a styrene -  
          butadiene - styrene block copolymer; and
- 70 to 90 % by weight of impact polystyrene  
20           grafted with maleic anhydride.

                  17. A composition according to Claim 1,  
substantially as described in any one of Examples 2 to  
25.

                  18. A method of making a multilayer  
25    composite which method comprises providing a layer of a  
composition as claimed in any of Claims 1 to 17 between  
a layer of polystyrene, polycarbonate or polyester and  
a layer of at least one resin chosen from polyolefins,

ethylene - vinyl alcohol copolymers, polyamides and polyesters.

19. A method according to Claim 18, wherein the three layers are coextruded.

5 20. A multilayer composite obtained by the method claimed in Claim 18 or 19.

21. A coextruded multilayer composite which composite comprises:

10 at least once the following succession of three layers:

- a layer of polystyrene, polycarbonate or polyester,
- a layer of a binder composition as claimed in any of Claims 1 to 17; and
- 15 - a layer of at least one resin chosen from polyolefins, ethylene - vinyl alcohol copolymers, polyamides and polyesters.

22. A composite according to Claim 21, which consists of one of the following layer combinations:

20 PS/binder/EVOH, PS/binder/PA, PS/binder/PET, PS/binder/PO, PS/binder/EVOH/binder/PS, and PS/binder/EVOH/binder/PO, PS/binder/EVOH/binder/PET, PS/binder/EVOH/PA/binder/PS, wherein PS = polystyrene, EVOH = ethylene-vinyl alcohol copolymer, PA =  
 25 polyamide, PET = poly(ethylene terephthalate) and PO = polyolefin.

**Relevant Technical Fields**

(i) UK Cl (Ed.N) C3M (MXAH, MXAN, MXAM); C3V (VAL, VAM)

(ii) Int Cl (Ed.) C09J

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE: WPI

Search Examiner  
K MACDONALD

Date of completion of Search  
27 JUNE 1995

Documents considered relevant following a search in respect of Claims :-  
1-22

**Categories of documents**

- |  |   |
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| <p><b>X:</b> Document indicating lack of novelty or of inventive step.</p> <p><b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.</p> <p><b>A:</b> Document indicating technological background and/or state of the art.</p> | <p><b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.</p> <p><b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.</p> <p><b>&amp;:</b> Member of the same patent family; corresponding document.</p> |
|--|---|

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2066270 A (ASAHI) Claim 1	at least Claim 1
X	GB 1576401 (ACC CHEMICAL) Claims 1, 17	at least Claim 1
X	GB 0747597 (US RUBBER CO) Claim 1; page 2 lines 77-85	at least Claim 1
X	EP 0389094 A2 (MORTON) page 3, lines 30-35	at least Claim 1
X	US 4007311 (SHELL) Claim 1	at least Claim 1
X	WPI Abstract Accession No 83-10578K/05 and JP 57205440 A (KOBUNSHI) 16.12.82 (see abstract)	at least Claim 1

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